Ultraviolet Photoemission Studies of Formaldehyde

and Related Molecules Adsorbed on Ru(110)

by

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ULTRAVIOLET PHOTOEMISSION STUDIES OF FORMALDEHYDE

AND RELATED MOLECULES ADSORBED ON Ru(110)

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I. INTRODUCTION

The adsorption of small organic molecules on surfaces is of importance in a variety of areas including catalysis, electronic devices, and lubrication. An important energy-related catalytic process is the methanation reaction ($3H_2 + CO \rightarrow CH_4 + H_2O$) which is used in the production of synthetic natural gas; one of the most active catalysts for this reaction is ruthenium.[1,2] Although the detailed mechanisms of the reaction are not known, it has been suggested that methanation proceeds via the formation of H_2CO or H_2CO-derived intermediates.[1] Recent Temperature Programmed Desorption studies (TPD) of H_2CO adsorbed on the Ru(110)*surface at 300 K demonstrate that small quantities of CH_4 are produced as a decomposition product.[3,4] In the present effort, we have used Ultraviolet Photoemission Spectroscopy (UPS) and TPD to characterize the adsorption and decomposition of H_2CO on Ru(110) at T ∿ 80 K; the atomic structure of the ideal Ru(110) surface is shown in the inset to Fig. 1.

In previous UPS studies, molecular H_2CO adsorption has been reported at ∿ 80 K on ZnO[5] and MoS$_2$ surfaces.[6] H_2CO has been reported to decompose on Pd films at 300 K,[7] and to form molecular multilayers on polycrystalline Pd at 120 K.[5] During thermal desorption studies of the decomposition products of H_2CO on Pd at T > 300 K, an attractive interaction between H(ads) and CO(ads) is observed.[8] The most extensive studies of H_2CO adsorption have been on W surfaces.[9-11] On W(100) at 300 K, adsorption appears to be dissociative at low coverages, but a molecular complex is present at higher coverages (θ ∿ 1 monolayer) as evidenced by TPD,[9] UPS,[10] and XPS[11] (X-ray Photoelectron Spectroscopy). Adsorption of H_2CO on W(100) at ∿ 80 K results in formation of a molecular complex as well as non-dissociatively adsorbed H_2CO.[11] To the best of our knowledge, there have been no previous

*We use the three-digit notation for the hexagonal crystal rather than the redundant four digit notation in which this face would be denoted (1120).

2

Fig. 1. Lower curve: work function change, $\Delta\phi$, as a function of H_2CO exposure on Ru(110) at 80 K. (1 L = 1 Langmuir = 1 x 10^{-6} Torr-sec.; 1 Torr = 133.3 N/m^2). Data from separate data runs are indicated by different symbols. The measurement uncertainty is indicated by the error bar in the center of the figure.

Upper curve: work function change, $\Delta\phi$, as a function of CO exposure on Ru(110) which was pre-covered by a monolayer of hydrogen; T = 80 K. Present measurements are shown as triangles; the crosses indicate the unpublished data of Sandstrom, et al. (Ref. 18). An inset at the right is a schematic of the atomic arrangement of the ideal Ru(110) surface.
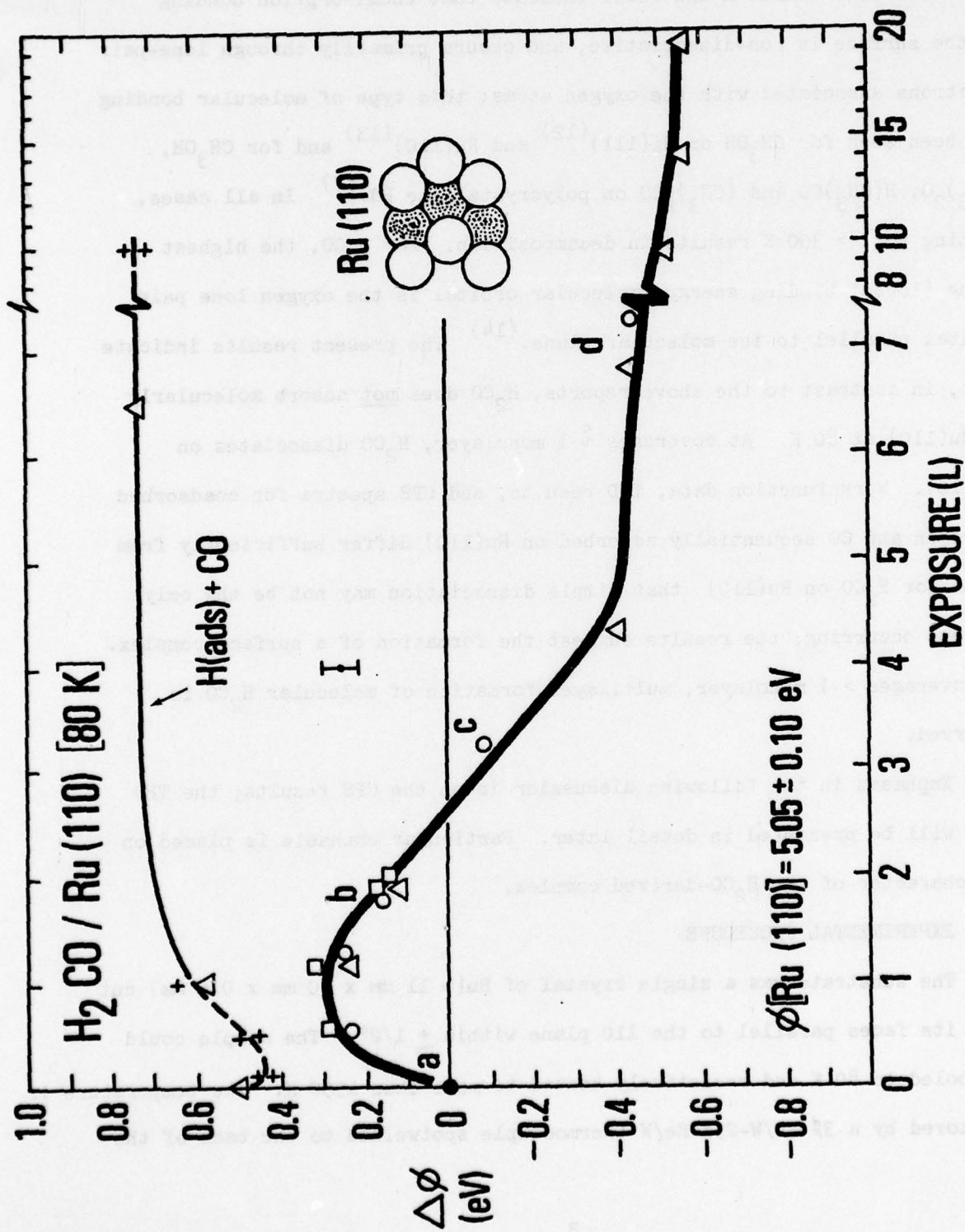
H₂CO / Ru(110) [80 K]

ϕ[Ru(110)] = 5.05 ± 0.10 eV

Ru(110)

H(ads) + CO

$\Delta\phi$ (eV)

EXPOSURE (L)

Fig. 1.

published UPS studies of the adsorption of fractional monolayers of H_2CO on clean metal surfaces at $T \sim 80$ K.

UPS studies of a number of oxygen-containing organic molecules on metal surfaces at 120 K and below indicate that chemisorption bonding to the surface is non-dissociative, and occurs primarily through lone-pair electrons associated with the oxygen atoms; this type of molecular bonding has been seen for CH_3OH on Ni(111)[12] and Ru(110)[13] and for CH_3OH, $(CH_3)_2O$, $H(CH_3)CO$ and $(CH_3)_2CO$ on polycrystalline Pd.[7] In all cases, heating to T > 300 K results in decomposition. For H_2CO, the highest lying (lowest binding energy) molecular orbital is the oxygen lone pair orbital parallel to the molecular plane.[14] The present results indicate that, in contrast to the above reports, H_2CO does not adsorb molecularly on Ru(110) at 80 K. At coverages $\stackrel{<}{\sim} 1$ monolayer, H_2CO dissociates on Ru(110). Work function data, TPD results, and UPS spectra for coadsorbed hydrogen and CO sequentially adsorbed on Ru(110) differ sufficiently from those for H_2CO on Ru(110) that simple dissociation may not be the only process occurring; the results suggest the formation of a surface complex. At coverages > 1 monolayer, multilayer formation of molecular H_2CO is observed.

Emphasis in the following discussion is on the UPS results; the TPD data will be presented in detail later. Particular emphasis is placed on the character of the H_2CO-derived complex.

II. EXPERIMENTAL PROCEDURE

The substrate was a single crystal of Ru(~ 11 mm x 10 mm x 0.5 mm) cut with its faces parallel to the 110 plane within $\pm 1/2°$. The sample could be cooled to 80 K and resistively heated to more than 1550 K. The temperature is monitored by a 3% Re/W-25% Re/W thermocouple spotwelded to the back of the

3

crystal. The crystal was cleaned by heating in O_2, followed by flashing to 1550 K. This procedure has been demonstrated using AES to produce clean Ru [15] and was verified for this crystal in a separate vacuum system.

The formaldehyde was prepared by the method of Yates, et. al. [9] and stored in a previously baked, mostly glass enclosure. Daily checks of its purity were made with the mass spectrometer. The exposures of all gases are based on measured areas of plots of mass spectrometer ion current vs. time. Hydrogen exposures were corrected for the known ion gauge sensitivity. [16] Fomaldehyde exposures are based on doses monitored using the mass 29 signal, with the Bayard-Alpert gauge off.

The precision of work function measurements based on photoemission thresholds is ± 0.05 eV.

The UHV system used in this experiment has been previously described and has a base pressure of $\sim 1 \times 10^{-10}$ Torr. [17] The electrons are excited by He I radiation ($h\nu$ = 21.2 eV) from a windowless microwave discharge lamp and are measured by a three-grid hemispherical retarding field energy analyzer with a collection solid angle of $\sim 0.6 \pi$ steradians and a resolution of 0.12 eV at 20 eV. [17] The typical experimental mode was as follows: (a) flash the sample clean at 1550 K, (b) measure its work function from the photoelectric threshold to check for cleanliness during the two minutes of cooling time to 80 K, (c) expose to a gas while monitoring the appropriate mass peak, (d) measure the UPS spectrum, and (e) heat the sample with an appropriate nearly linear temperature ramp while measuring the total pressure and the TPD of a mass peak of interest.

III. RESULTS

A. Work Function Changes for H_2CO and H_2 + CO Adsorbed at 80 K

The measurement of work function changes during adsorption is a

4

useful monitor of charge transfer in the adsorbed layer on the surface.

The work function of clean Ru(110) was found from the photoelectric threshold in repeat experiments to be 5.05 ± 0.10 eV. The lower solid curve in Fig. 1 is a plot of the surface work function change ($\Delta\phi = \phi_{covered} - \phi_{clean}$) as a function of exposure to H_2CO at 80 K. The work function change rises to a maximum (∼ 0.3 eV) at low exposures. For higher exposures, $\Delta\phi$ shows a negative slope and decreases to a saturation value above 5 L (1 L = 1 Langmuir = 1 x 10^{-6} Torr-sec). The limiting value of $\Delta\phi$ = - 0.55 eV is characteristic of an H_2CO multilayer on Ru(110). These $\Delta\phi$ versus exposure data are very similar to results obtained previously for H_2CO adsorption on W(111) and W(100).[9] There, also, $\Delta\phi$ increased at low exposures and achieved negative values at high exposures.

For comparison, we include in Fig. 1 a plot of changes in $\Delta\phi$ when a monolayer of hydrogen on Ru(110) at 80 K ($\Delta\phi$ = 0.5 eV) is exposed to increasing doses of CO. The present data, in conjunction with the unpublished data of Sandstrom, et al.,[18] indicate that $\Delta\phi$ passes through a shallow minimum at low exposures, and rises to a limiting value of $\Delta\phi$ = 0.7 eV at high exposures, when the surface is saturated with H_2 + CO. At 80 K, CO displacement of adsorbed hydrogen from the surface is slight, but preadsorption of CO allows only minimal amounts of hydrogen to adsorb subsequently. The limiting value of $\Delta\phi$ for the H_2 + CO saturated surface is between the value $\Delta\phi \gtrsim$ 1.0 eV observed for a CO monolayer and that seen for adsorbed hydrogen. A minimum in a plot of $\Delta\phi$ vs. CO exposure has also been seen for the average work function change of a hydrogen covered Ru field emitter[19] at 300 K.

The data of Fig. 1 suggest the possibility that adsorbed H_2CO and sequentially adsorbed hydrogen and CO exhibit similar surface dipole characteristics at low exposures (and low coverages), since the sign of $\Delta\phi$ is the

5

same in both cases. At higher exposures, however, the decrease in $\Delta\phi$

for adsorbed H_2CO suggests that simple dissociation into coadsorbed hydrogen + CO

would no longer occur. It has been suggested previously for H_2CO on W(100)

and W(111)[9] that such work function behavior might arise for H_2CO dis-

sociation at low coverages, with the formation of a surface complex or

undissociated H_2CO at higher exposures. Indeed, the UPS results for a

saturation coverage of H_2CO on Ru(110) discussed in Section III.B. indicate

the presence of molecular H_2CO, but its existence may not be the complete

explanation of the work function variation with H_2CO exposure. This

variation in $\Delta\phi$ may also involve the population of different surface

bonding sites: a "smoothing" effect at low coverages as the (110) trough

sites are filled, followed by adsorption at sites atop the (110) ridges.

Whatever the reasons for the detailed shape of these curves, it is clear

that H_2CO for exposures > 1 L does not behave like coadsorbed H_2 + CO.

 B. Ultraviolet Photoemission Spectra for H_2CO and Related Molecules
   Adsorbed at 80 K

    A series of unsmoothed UPS spectra for H_2CO adsorbed on Ru(110)

at 80 K are shown in Fig. 2 as excited by 21.2 eV radiation. For clarity,

smooth curves replace the data in parts of some spectra. Curve a is the energy

distribution curve for the clean Ru surface. The structure in the range

0 to 6 eV is due to photoemission from the Ru(4d,5s) band, and the region

from 6 to 14 eV is relatively structureless. This is consistent with UPS

data for Ru(001)[20] and Ru(100).[21] Following adsorption of H_2CO doses of

1.8 L and 3.2 L, respectively, curves b and c were measured. These curves

are associated with fractional monolayer coverages of H_2CO, and correspond

to the labeled points of Fig. 1. In both cases, new features at ~ 7.5 and

~ 11 eV are seen for higher exposures. The intense spectrum of curve d

exhibits new features unlike those of curves b and c, and appears to be

6

Fig. 2. Unsmoothed UPS spectra (hν = 21.2 eV) for clean Ru(110) (curve a) and for
increasing formaldehyde exposures on Ru(110) at 80 K (curves b-d).
The exposures are indicated on the figure. Each spectrum required
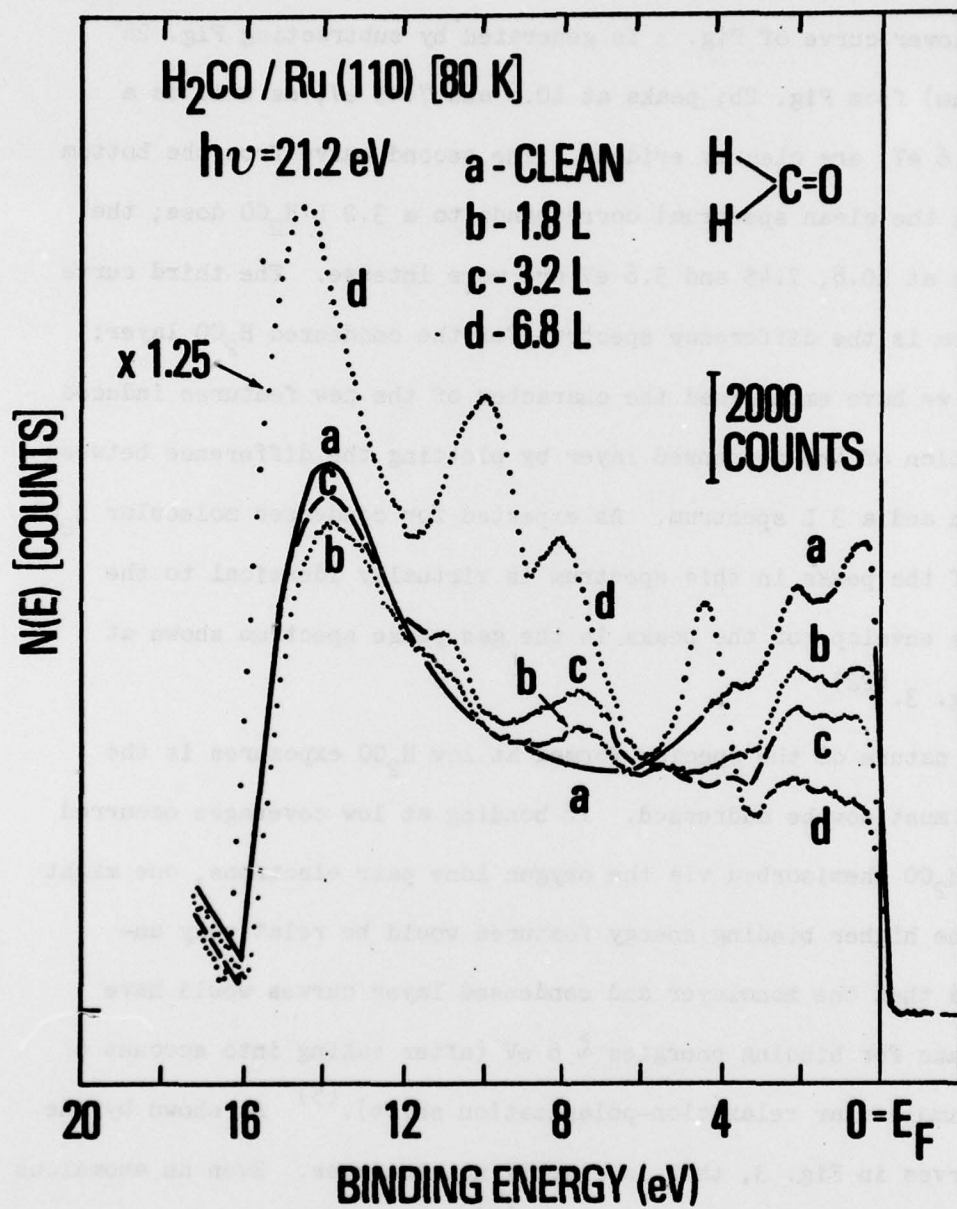8 scans of 256 channels, 0.2 sec/channel.

H₂CO / Ru (110) [80 K]

hν = 21.2 eV

a - CLEAN
b - 1.8 L
c - 3.2 L
d - 6.8 L

H
   C=O
H

x 1.25

2000
COUNTS

N(E) [COUNTS]

20   16   12   8   4   0 = E_F

BINDING ENERGY (eV)

Fig. 2.

characteristic of a condensed H_2CO layer (point d, Fig. 1).

The chemisorption-induced features in the UPS spectra of Fig. 2 are more clearly seen in the UPS difference spectra shown in Fig. 3; features at binding energies below 13 eV are related to differences in work function values. The lower curve of Fig. 3 is generated by subtracting Fig. 2a (clean spectrum) from Fig. 2b; peaks at 10.8 and 7.45 eV, as well as a shoulder at 5.6 eV, are clearly evident. The second curve from the bottom (Fig. 2c minus the clean spectrum) corresponds to a 3.2 L H_2CO dose; the three features at 10.8, 7.45 and 5.6 eV are more intense. The third curve from the bottom is the difference spectrum for the condensed H_2CO layer; in this case, we have emphasized the character of the new features induced by the adsorption of the condensed layer by plotting the difference between a 7 L spectrum and a 3 L spectrum. As expected for condensed molecular H_2CO, the spacing of the peaks in this spectrum is virtually identical to the spacing of the envelope of the peaks in the gas phase spectrum shown at the top of Fig. 3.[22]

The nature of the species formed at low H_2CO exposures is the problem which must now be addressed. If bonding at low coverages occurred as molecular H_2CO chemisorbed via the oxygen lone pair electrons, one might expect that the higher binding energy features would be relatively un-perturbed, and that the monolayer and condensed layer curves would have coincident peaks for binding energies $\gtrsim$ 6 eV (after taking into account a constant extramolecular relaxation-polarization shift).[5] As shown by the difference curves in Fig. 3, this is clearly not the case. Even an anomalous extramolecular relaxation-polarization shift[5] of the H_2CO in-plane π_x orbital (the highest B.E. peak in the He I gas phase spectrum) for chemisorbed molecular H_2CO cannot be invoked to argue that chemisorbed, molecular H_2CO

7

is adsorbed at 80 K on Ru(110). We conclude from Fig. 3 that H_2CO is not molecularly adsorbed in the submonolayer coverage range, and suggest that low coverage H_2CO is, to a large extent, dissociated.

In order to shed light on the nature of the H_2CO decomposition products, we compare in Figure 4 the UPS difference spectrum for a 1.8 L H_2CO dose on Ru(110) with difference spectra for coadsorbed hydrogen + CO, adsorbed CO alone, and adsorbed hydrogen alone on Ru(110). The adsorption of a saturation coverage of hydrogen results in the appearance of two peaks at 5.6 and 1.65 eV below E_F, as well as selective attenuation of the Ru valence band. The CO difference spectrum shows the characteristic two-peaked structure observed for the chemisorption of molecular CO on many surfaces and in particular, other faces of Ru;[20,21] the peak at 10.6 eV is due to the CO 4σ level, and the peak at 7.5 eV is due to a combination of the 5σ and 1π levels. Curve 4b corresponds to coadsorbed hydrogen + CO on Ru(110); a saturation hydrogen layer was exposed to a 1.2 L dose of CO. It exhibits four features which have peak energies within 0.1 eV of those found in the separate hydrogen and CO spectra. Curve 4a corresponds to a fractional monolayer coverage (1.8 L dose) of H_2CO. This H_2CO spectrum is quite different from that of molecular H_2CO (Fig. 3) and similar to the coadsorbed H_2 + CO spectrum (Fig. 4b), indicating that a major portion of the adsorbed H_2CO is dissociated. However, there are two notable differences between Figs. 4a and 4b. Firstly, the peak at 10.8 eV in the H_2CO spectrum is broader than and is shifted by $\sim$ 0.3 eV with respect to the corresponding feature in the H_2 + CO curve. Secondly, the strong peak at 1.65 eV, related to hydrogen adsorption in the H_2 + CO spectrum, is not evident in the H_2CO spectrum. These differences appear more significant in light of the thermal behavior of adsorbed H_2CO.

8

Fig. 3. UPS spectrum for gas phase formaldehyde (Ref. 22) and unsmoothed

difference spectra [N(E)] for H_2CO adsorbed on Ru(110) at 80 K

($h\nu$ = 21.2 eV). The upper gas phase photoelectron spectrum is re-

ferenced to the ionization potential (I.P.) relative to the vacuum

level. The multilayer curve is the difference between UPS spectra for

a 7 L and a 3 L H_2CO exposure on Ru(110) at 80 K. Curves labeled

(c-a) and (b-a) refer to the difference spectra for the data shown

in Fig. 2.

Fig. 3. Vertical UPS str... ... the adsorption of various gases
Ru(110) at 80 K. The exposures ... ... exposures corresponding to each
curve are (a) 1.8 L of H₂CO; (b) ... ... O₂, followed by
adsorption of 1.7 L of H₂; (c) 2.2 L of H₂CO; ... 1 L of H₂.
Each difference spectrum was obtained ... subtracting the clean
surface spectrum from ... adsorbate-covered spectrum. Each
spectrum required 8 scans of 256 channels of 8 sub-channel.
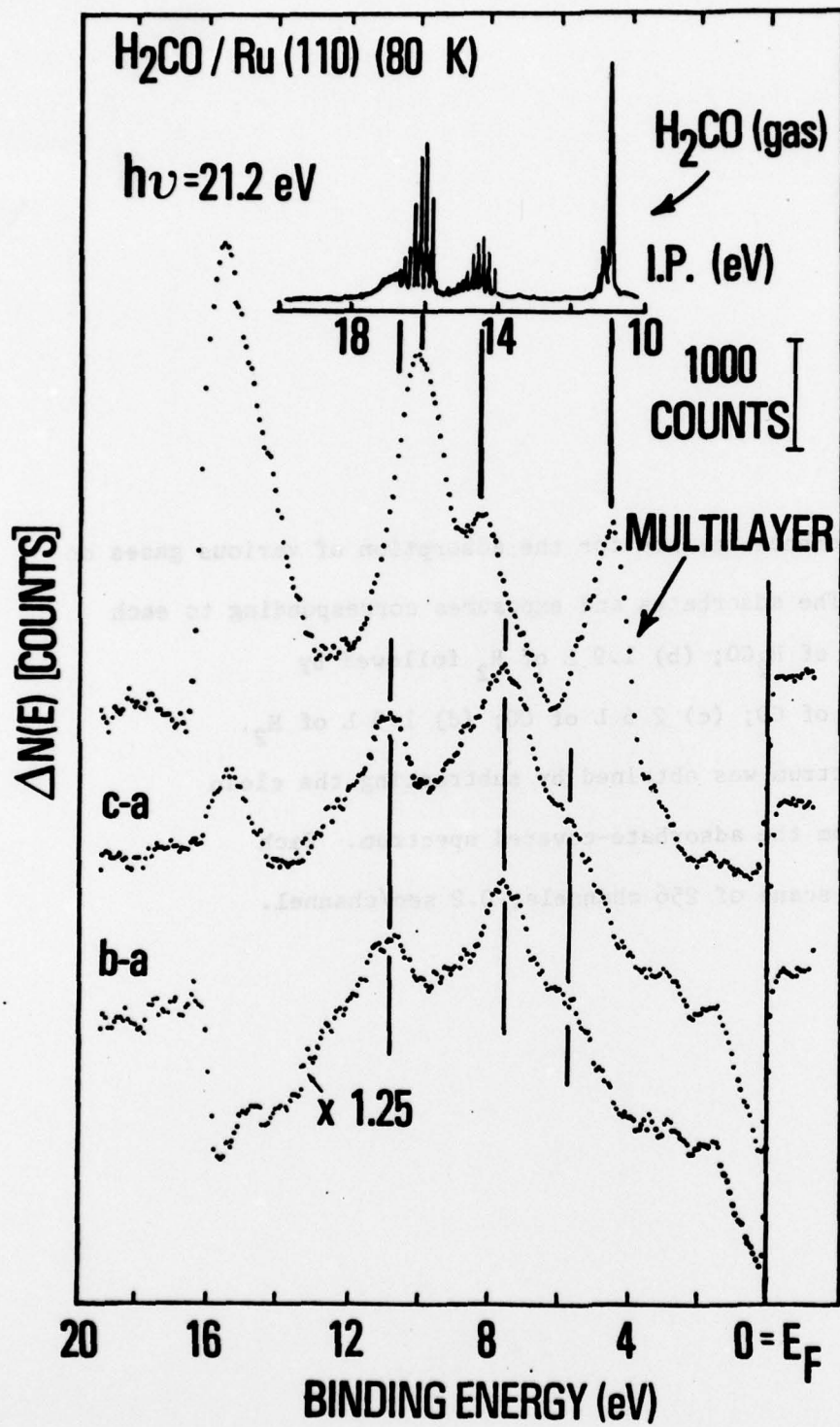
Fig. 3.

Fig. 4. Unsmoothed UPS difference spectra for the adsorption of various gases on Ru(110) at 80 K.   The adsorbates and exposures corresponding to each curve are (a) 1.8 L of H_2CO; (b) 1.9 L of H_2 followed by adsorption of 1.2 L of CO; (c) 2.6 L of CO; (d) 1.9 L of H_2. Each difference spectrum was obtained by subtracting the clean surface spectrum from the adsorbate-covered spectrum. Each spectrum required 8 scans of 256 channels, 0.2 sec/channel.
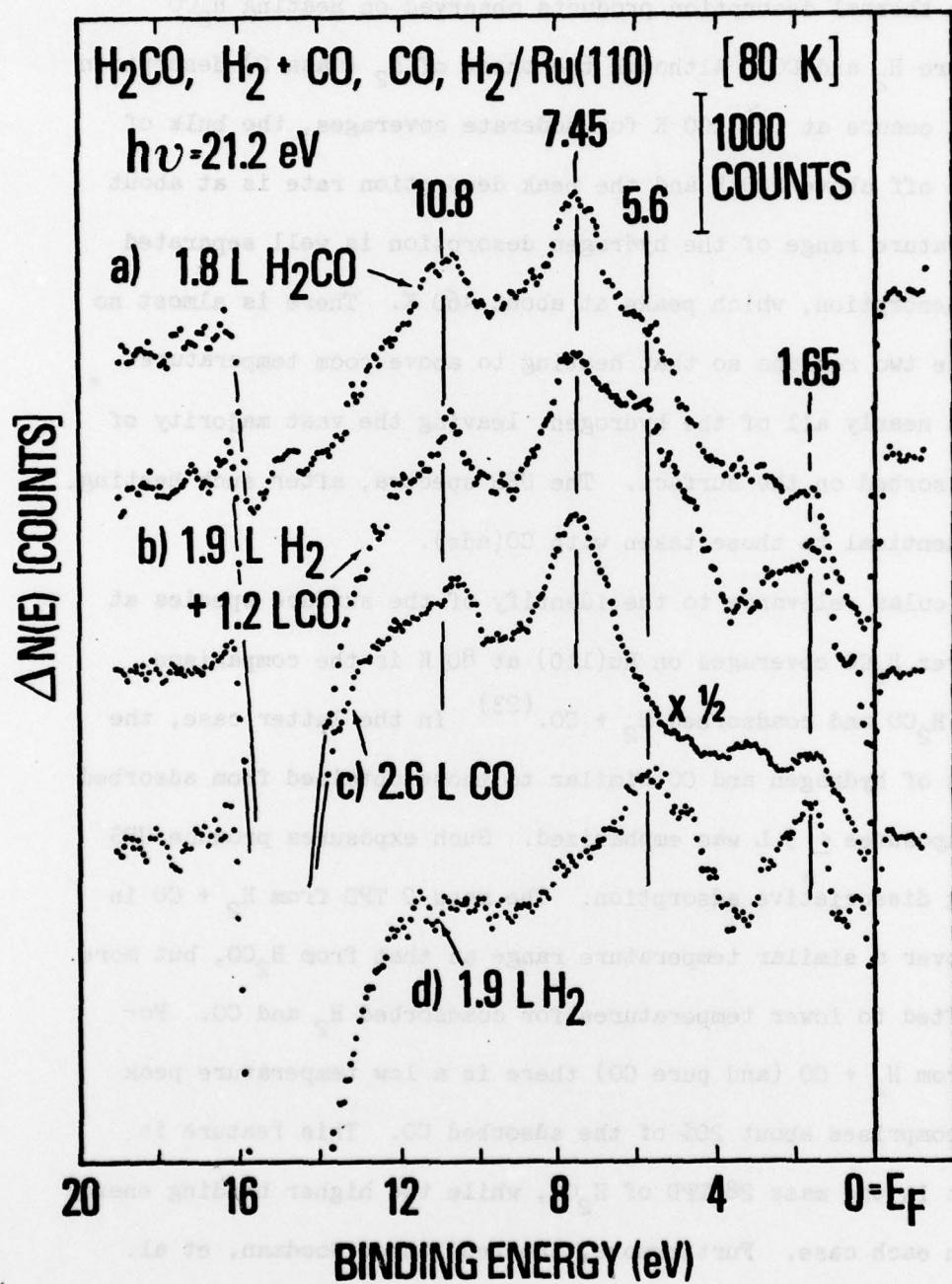
H$_2$CO, H$_2$ + CO, CO, H$_2$/Ru(110)   [80 K]

hν = 21.2 eV

1000 COUNTS

ΔN(E) [COUNTS]

10.8   7.45   5.6

a) 1.8 L H$_2$CO

1.65

b) 1.9 L H$_2$ + 1.2 L CO

X ½

c) 2.6 L CO

d) 1.9 L H$_2$

20   16   12   8   4   0 = E$_F$

BINDING ENERGY (eV)

Fig. 4.

C. Thermal Desorption Results for H_2CO and H_2 + CO Adsorbed at 80 K

The main thermal desorption products observed on heating H_2CO adsorbed at 80 K are H_2 and CO. Although the onset of H_2 (mass 2) desorption from adsorbed H_2CO occurs at $T \gtrsim$ 100 K for moderate coverages, the bulk of the hydrogen comes off above 200 K and the peak desorption rate is at about 270 K. The temperature range of the hydrogen desorption is well separated from that for CO desorption, which peaks at about 460 K. There is almost no overlap between the two regions so that heating to above room temperature ($\sim$ 330 K) removes nearly all of the hydrogen, leaving the vast majority of the CO still chemisorbed on the surface. The UPS spectra, after such heating, are essentially identical to those taken with CO(ads).

Of particular relevance to the identify of the surface species at fractional monolayer H_2CO coverages on Ru(110) at 80 K is the comparison of TPD studies of H_2CO and coadsorbed H_2 + CO.[23] In the latter case, the study of coverages of hydrogen and CO similar to those obtained from adsorbed H_2CO layers for exposures $\leq$ 3 L was emphasized. Such exposures produce UPS spectra indicating dissociative adsorption. The mass 2 TPD from H_2 + CO in this case occurs over a similar temperature range as that from H_2CO, but more desorption is shifted to lower temperatures for coadsorbed H_2 and CO. For the mass 28 TPD from H_2 + CO (and pure CO) there is a low temperature peak ($\sim$ 150 K) which comprises about 20% of the adsorbed CO. This feature is essentially absent in the mass 28 TPD of H_2CO, while the higher binding energy peak is similar in each case. Furthermore, the results of Goodman, et al. show that small quantities of CH_4 and other molecular products can thermally desorb from a fractional H_2CO monolayer on Ru(110) adsorbed at about 300 K,[3,4] but cannot be produced by thermal desorption of coadsorbed hydrogen + CO. Thus, as with the UPS results, there are rough similarities and more subtle

9

differences between the TPD of H_2 + CO and H_2CO adsorbed on Ru(110). There is an attractive interaction which holds some portion of the hydrogen and CO on the surface to higher temperatures than is the case for a coadsorbed layer of H_2 + CO. This suggests the possibility of a surface molecular complex existing for at least some of the dissociated H_2CO, but it is not possible to assess the importance of other factors such as differences in binding sites for the two situations.

IV. DISCUSSION

In the spectral region between 4 and 12 eV below E_F in Figure 3, CO adsorbed at low coverages at 80 K produces a species whose UPS difference spectrum is distinct from molecular formaldehyde. In contrast, although several molecular orbitals of chemisorbed H_2CO on ZnO were perturbed by the interaction with the surface,[5] the molecular character of the adsorbate was demonstrable. However, the distortion of the UPS spectrum is so great on the Ru(110) surface that using the H_2CO molecular orbital structure as a "finger-print" is not useful. In fact, we conclude that low coverages of H_2CO dissociate on the Ru(110) surface at 80 K; H_2CO is the first organic molecule incorporating oxygen which has been observed using UPS techniques to dissociate at such low temperatures on a metal. At somewhat higher temperatures, between 100 K and 120 K, we note that carbon-carbon bond scission is reported to occur upon the adsorption of C_2H_2 and C_2H_4 on the clean α-Fe(100) surface.[24]

In contrast to its low exposure behavior on Ru(110), for high exposures of H_2CO the surface with a saturated work function value of $\Delta\phi$ = -0.55 eV exhibits peak molecular orbital energies with such a clear resemblance to those of the gas phase photoelectron spectrum of H_2CO that we conclude this layer contains pure molecular H_2CO.

The question of the nature of the dissociated species of adsorbed H_2CO at 80 K remains. If we are to use the "fingerprint" method of identification,

the overall similarities between the fractional monolayer formaldehyde spectrum and a spectrum produced by coadsorption of hydrogen + CO is compelling (Fig. 4). Although the relative intensities do not match exactly, the strong peak at 7.5 eV and a lesser one in the 10.8 eV region are suggestive that a CO bond exists with the carbon atom bonded to the surface. The presence of a shoulder at 5.6 eV coincides with the dominant hydrogen-related feature. In addition, the $\Delta\phi$ values for very low formaldehyde coverages and coadsorbed hydrogen + CO are both positive (indicating electro-negative species; cf. Fig. 1), and differ by as little as 0.15 eV. Furthermore, the gross features of the desorption of H_2 and CO from H_2CO are quite similar to those of H_2 + CO.

From the UPS results the dominant impression is certainly that low coverage adsorbed H_2CO looks like H_2 + CO. However, the differences we observe between the two, although small, may be important in light of the TPD and work function change data. The feature at 1.65 eV in both the H_2 and H_2 + CO UPS curves is absent in any strength in the H_2CO curve (Fig. 4). This feature is also absent following heating of adsorbed H_2CO or CH_3OH[12] layers on Ru(110) to $\gtrsim$ 200 K, where one would expect complete dissociation to coadsorbed H_2 + CO. (It should be cautioned that the dependence of this feature on hydrogen coverage in the presence of CO is not known.) We have also noted that there is a difference in the separation of the main peaks ($\sim$ 0.3 eV) and a broader, more symmetric shape to the 10.8 eV features in the H_2CO spectrum, when compared to corresponding features in the H_2 + CO spectrum or the CO spectrum.

The thermal desorption studies also exhibit differences between H_2CO and H_2 + CO in a shift of hydrogen binding states to higher energy and the absence of the low temperature CO peak in the TPD of adsorbed H_2CO.

11

The differences in $\Delta\phi$ for H_2CO and H_2 + CO in the later stages of monolayer formation (2-4 L, Fig. 1) indicate the presence of different surface species in the two cases. The possibility of an H_2CO-derived complex is suggested, but its concentration cannot be estimated from these data.

In conclusion, H_2CO is observed to adsorb dissociatively on Ru(110) at 80 K. The work function and TPD data, supported by subtle changes in the UPS spectra, suggest that the H_2CO-derived surface species are not solely identified with coadsorbed hydrogen + CO. At least a portion of the H and CO present on the surface is interacting differently than in a H_2 + CO layer. This may indicate the existence of a surface molecular complex, but a better description of this interaction must await additional surface spectroscopic measurements.

V. ACKNOWLEDGMENT

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